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**(54) Method of removing CO from CO + H<sub>2</sub> gases and fuel cell system using method**

Verfahren zum Entfernen von CO aus einem CO + H<sub>2</sub> enthaltenden Gasgemisch und Brennstoffzellensystem mit Verwendung derselben

Méthode pour l'élimination de CO d'un mélange gazeux CO + H<sub>2</sub> et système de piles à combustible utilisant cette méthode

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## Description

[0001] The present invention relates to a method for reducing the CO content of a CO-containing hydrogen-rich gas mixture, more especially to render the gas mixture more suitable for use in fuel cell systems.

[0002] Fuel cells are devices that convert fuel and oxidant to electrical energy. Most efficient fuel cells use pure hydrogen as the fuel and oxygen as the oxidant. Unfortunately use of pure hydrogen has a number of known disadvantages not the least of which is its relatively high cost. Consequently, attempts have been made to operate fuel cells using other than pure hydrogen as the fuel. For example, attempts have been made to use hydrogen-rich gas mixtures obtained from steam reforming methanol as a fuel cell feed. These attempts, however, have not resulted in a practical system because carbon monoxide which is present in such gas mixtures degrades cell performance, even in relatively low concentrations.

[0003] JP-A-3208801 relates to contacting a CO-containing, hydrogen stream in a separator with a platinum-on-alumina adsorbent, to selectively adsorb CO. The adsorbed CO is oxidised to CO<sub>2</sub> and the treated hydrogen stream is suitable for use with a membrane-type fuel cell. Operation based on the alternate use of two separators is also referred to.

[0004] JP-A-3093602 relates to the selective removal of CO from a CO-containing hydrogen stream by contact with a catalyst of ruthenium on alumina, silica or magnesia.

[0005] It is an object of the present invention to treat a CO-containing, hydrogen-rich gas mixture to lower the CO content of the mixture to render it more suitable for use in fuel cell systems.

[0006] It is another object of the present invention to provide a method for lowering the CO content of a CO-containing hydrogen-rich gas stream in a single step.

[0007] It is another object of the present invention to provide a method for reducing the CO content of a CO-containing hydrogen-rich gas stream which is energy efficient.

[0008] Another object of the present invention is to provide a fuel cell system in which a CO-containing, hydrogen-rich gas stream is subjected to an adsorption step and in which the carbon monoxide is preferentially adsorbed, thereby lowering the carbon monoxide content of the gas mixture, e.g., to below about 10 ppm, to provide a substantially CO-free, hydrogen-rich gas stream which is subsequently fed to the fuel cell for use therein.

[0009] Simply stated, the present invention comprises a method for lowering the carbon monoxide content of a CO-containing, hydrogen-rich gas stream by contacting the gas stream with an adsorbent capable of preferentially adsorbing the carbon monoxide in the gas stream, the adsorbent being selected from the carbides and nitrides of tungsten, molybdenum, vanadium, chro-

mium, tantalum and mixtures thereof. Preferably the adsorbent will have a surface area from 0.5 to about 200 m<sup>2</sup>/gm.

[0010] The present invention also involves a fuel cell system comprising a fuel cell including an anode, a cathode and an electrolyte arranged in operative association with a carbon monoxide separator. The system includes means for bringing a CO-containing hydrogen rich gas in contact with the carbon monoxide separator to provide a substantially carbon monoxide free, hydrogen-rich gas and means to feed the substantially CO-free gas to the anode of the fuel cell. The separator contains an adsorbent selected from the carbides and nitrides of tungsten, molybdenum, vanadium, chromium, tantalum and mixtures thereof. Preferably the system includes means for periodically feeding a desorbent gas to the separator to desorb absorbed carbon monoxide thereby regenerating the adsorbent.

[0011] The adsorbent may be supported or unsupported. Suitable supports are any of those known in the art of catalysis and include those selected from one or more of the following: silicas, aluminas, silica-aluminas, titanias, aluminosilicates, carbon. Unsupported metal adsorbents may be made by any suitable technique. A suitable technique is that known as the Raney method, e.g., as described by M. Raney, Ind. Eng. Chem., vol. 32, page 1199, 1940 and H. Krupp et al, J. Electrochem. Soc., volume 109, page 553, 1962.

[0012] These and other embodiments of the present invention will be described in the following detailed description.

[0013] Figure 1 is a schematic illustration of a fuel cell system including a CO separator utilizing a selective adsorbent in accordance with this invention.

[0014] Figure 2 is a schematic illustration of an alternate embodiment of the invention employing two CO separators in combination with a fuel cell.

[0015] The present invention has wide applicability in providing substantially CO-free, hydrogen-rich gas streams; however, the invention is particularly adapted to providing a substantially CO-free, hydrogen-rich gas stream for use in fuel cells. Therefore, the present invention will be described with particular reference to fuel cell systems.

[0016] In general, the gas stream used in the present invention will be obtained by the well-known process of steam reforming a hydrocarbon or an alcohol such as methanol and thereafter subjecting the product gas stream to the equally well-known carbon monoxide shift reaction. The resultant gas stream typically will contain about 0.5% CO. Alternatively, the gas stream may be obtained by partial oxidation of hydrocarbons, especially methane.

[0017] Referring now to Figure 1, a fuel cell device 10 has been illustrated, for the sake of simplicity, as consisting of a single cell having an anode side or compartment 11 and a cathode side or compartment side 12. A supply line 14 is provided for supplying an oxidant, such

as oxygen or air, to the cathode side 12 of the cell. Operably connected to the fuel cell 10 is a carbon monoxide removal apparatus or separator 20. The carbon monoxide removal apparatus 20 is provided with an inlet conduit 15 for introducing a CO-containing, hydrogen-rich reformer gas mixture into the apparatus 20.

[0018] As shown in the Figure 1 embodiment, the apparatus 20 contains a bed of solid material 21 capable of selectively adsorbing carbon monoxide in gas mixtures. A conduit 16 is provided for the passage of substantially CO-free, hydrogen-rich gas from the apparatus 20 to the anode compartment 11 of fuel cell 10. The apparatus 20 also includes a conduit 17 for introducing a sweep gas (e.g., steam) into the separator 20 for desorbing carbon monoxide adsorbed on solid material 21. Also, a conduit 18 is provided for removal of the desorbed carbon monoxide.

[0019] In operation, a CO-containing, hydrogen-rich gas stream, such as that previously described, is introduced via a conduit 15 into apparatus 20 for contact with the CO-adsorbent material 21 therein. The purified gas, which is substantially free of carbon monoxide, is removed via line 16 and fed to the anode compartment 11 of fuel cell 10. Prior to the complete utilization of the adsorbent capacity of solid 21, the flow of the gas into the apparatus 20 is terminated and a sweep or desorbent gas, such as steam, gaseous hydrocarbons (e.g. CH<sub>4</sub> streams), flue gas from combustion, and any suitable mixture thereof, is introduced via line 17 into the bed to desorb the CO adsorbed therein. In one embodiment of the present invention, an oxygen containing gas, such as air, is introduced into bed 21 with the sweep gas thereby oxidizing the adsorbed CO to CO<sub>2</sub> for removal. In a preferred embodiment, however, a generally non-oxidizing sweep gas is used, the CO and steam are removed from the separator 20 via line 18 and preferably are recycled to a steam reformer.

[0020] After regeneration of the adsorbent solid 21 in separator 20 is complete, flow of sweep gas is terminated and a CO-containing gas is again introduced into apparatus 20 via line 15. The CO-free gas stream is then fed via line 16 to anode compartment 11. This procedure can be repeated periodically as desired.

[0021] In an alternate embodiment of the present invention shown in Figure 2, two separators 30 and 40 are provided, each containing an adsorbent material 21 capable of selectively adsorbing carbon monoxide. The hydrogen-rich, carbon monoxide gas to be treated is introduced alternately to separators 30 and 40 via line 35. The treated gas having substantially all of the CO removed is discharged alternately from the adsorbers 30 and 40 via line 36 and is sent to anode compartment 11 of fuel cell 10.

[0022] Periodically, the separators 30 and 40 must be purged or reactivated to remove the adsorbed carbon monoxide from the adsorbent. This purging is done by introducing a sweep gas, such as steam, via line 37. The sweep gas will flow through adsorbers 30 or 40, as the

case may be, and be removed via line 38. The various valves 22 through 29 are operated in appropriate sequence to permit the alternate use of separators 30 and 40. For example, when valves 24 and 26 are open and valves 25, 27, 22 and 29 are closed, the CO-containing, hydrogen-rich gas introduced via line 35 will flow through the adsorbent material 21 in separator 40 and pass via line 36 into the anode compartment 11 of fuel cell 10. Before complete utilization of the adsorbent capacity of the adsorbent material 21 in separator 40, valves 24 and 26 will be closed and valves 25 and 27 will be open permitting the flow of reformer gas through the adsorbent material 21 in separator 30. At the same time with valves 28 and 23 closed and valves 22 and 29 open, a sweep gas such as steam, is introduced via line 37 and will flow through the separator 40 for discharge through line 38. Optionally and preferably the desorbed CO-containing gas is recycled to a steam reformer for the generation of additional hydrogen; however, it may be oxidized to CO<sub>2</sub> and otherwise disposed of.

[0023] In the practice of the present invention the adsorbent 21 is one which is capable of selectively adsorbing CO in a reformer gas stream to provide a hydrogen rich gas stream containing less than about 10 ppm CO and preferably below about 1 ppm and preferably to a stream totally free of CO. Solid adsorbents useful are the carbides and nitrides of tungsten, molybdenum, vanadium, chromium, tantalum and mixtures thereof. The preferred adsorbents will have a surface area in the range of about 0.5 to about 200 m<sup>2</sup>/gm. Especially preferred are the carbides and nitrides of tungsten and molybdenum.

[0024] The amount of adsorbent used will depend of course upon the CO content of the gas stream to be treated, the gas flow rate and the desired length of time to elapse before desorption is required. Typically, the CO-containing gas stream will be processed at pressures of from about 0.51 to 10.13 bar (0.5 to about 10 atmospheres) at temperatures in the range of about 25°C to about 500°C. Preferred pressure and temperature ranges are 1.01 to 5.07 bar (1 to 5 atmospheres) and 70°C to 300°C, respectively.

[0025] While the present invention has been illustrated and described as embodied in a particular arrangement of a selective CO-adsorbing apparatus for use in removal of CO from a gaseous fuel being supplied to a fuel cell, it should be appreciated that the present invention is not limited to this particular example. Rather, the scope of the present invention is to be determined in accordance with the appended claims.

#### Claims

1. A method for removing CO from a CO-containing, hydrogen-rich gas stream to provide a substantially CO-free, hydrogen-rich gas stream comprising:

passing the CO-containing, hydrogen-rich gas stream through an adsorbent capable of selectively adsorbing CO and selected from the carbides and nitrides of tungsten, molybdenum, vanadium, chromium, tantalum and mixtures thereof, whereby a substantially CO-free, hydrogen-rich gas stream is obtained.

2. The method of claim 1, wherein the adsorbent has a surface area in the range of from 0.5 to 200 m<sup>2</sup>/gm.
3. The method of claim 1 or claim 2, wherein the adsorbent is supported and/or unsupported.
4. The method of claim 3, wherein the support for the adsorbent is selected from one or more of silicas, aluminas, silica-aluminas, titanias, aluminosilicates and carbon.
5. The method of claim 4, wherein the adsorbent is tungsten carbide or molybdenum carbide.
6. The method of any preceding claim, further comprising the step of periodically desorbing CO from the adsorbent by means of a sweep or desorbent gas, which gas is, preferably, non-oxidizing for CO.

7. A fuel cell system comprising:

a fuel cell having an anode compartment and a cathode compartment;

at least one separator containing an adsorbent capable of selectively adsorbing CO from a CO-containing, hydrogen-rich gas stream, which adsorbent is selected from the carbides and nitrides of tungsten, molybdenum, vanadium, chromium, tantalum and mixtures thereof, for producing a substantially CO-free, hydrogen-rich gas stream;

a conduit for feeding a CO-containing, hydrogen-rich gas stream to the separator;

a conduit operably connecting the separator to the anode compartment of the fuel cell, for delivering the substantially CO-free, hydrogen-rich gas stream thereto; and

a conduit for feeding an oxidant to the cathode compartment.

8. The system of claim 7, including two said separators.
9. The system of claim 7 or claim 8, including a conduit for feeding a sweep gas to the (respective) separa-

tor to desorb adsorbed CO.

10. The system of any one of claims 7 to 9, wherein the adsorbent is supported and/or unsupported.

11. The system of claim 10, wherein the support for the adsorbent is selected from one or more of silicas, aluminas, silica-aluminas, titanias, aluminosilicates and carbon.

12. The system of any one of claims 7 to 11, wherein the adsorbent has a surface area in the range of from 0.5 to 200 m<sup>2</sup>/gm.

13. The system of any one of claims 7 to 12, wherein the adsorbent is tungsten carbide or molybdenum carbide.

## 20 Patentansprüche

1. Verfahren zur Entfernung von CO aus einem CO-enhaltenden, wasserstoffreichen Gasstrom, um einen im wesentlichen CO-freien, wasserstoffreichen Gasstrom zu erhalten, bei dem

der CO-enhaltende, wasserstoffreiche Gasstrom durch ein Adsorptionsmittel geführt wird, das in der Lage ist, selektiv CO zu adsorbieren und ausgewählt ist aus den Carbiden und Nitriden von Wolfram, Molybdän, Vanadium, Chrom, Tantal und Mischungen derselben, wobei ein im wesentlichen CO-freier, wasserstoffreicher Gasstrom erhalten wird.

2. Verfahren nach Anspruch 1, bei dem das Adsorptionsmittel eine Oberfläche im Bereich von 0,5 bis 200 m<sup>2</sup> pro Gramm aufweist.

3. Verfahren nach Anspruch 1 oder Anspruch 2, bei dem das Adsorptionsmittel auf einem Träger vorliegt und/oder trägerlos ist.

4. Verfahren nach Anspruch 3, bei dem der Träger für das Adsorptionsmittel ausgewählt ist aus einem oder mehreren von Siliciumdioxiden, Aluminiumoxiden, Siliciumoxid/Aluminiumoxiden, Titanoxiden, Aluminosilikaten und Kohlenstoff.

5. Verfahren nach Anspruch 4, bei dem das Adsorptionsmittel Wolframcarbid oder Molybdäncarbid ist.

6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem ferner periodisch CO von dem Adsorptionsmittel mittels eines Spülungs- oder Desorptionsgases desorbiert wird, wobei das Gas vorzugsweise für CO nicht oxidierend ist.

## 7. Brennstoffzellensystem, das umfaßt

eine Brennstoffzelle mit einem Anodenkompartiment und einem Kathodenkompartiment,

mindestens einen Separator, der ein Adsorptionsmittel enthält, das in der Lage ist, CO selektiv aus einem CO-enhaltenden, wasserstoffreichen Gasstrom zu adsorbieren, wobei das Adsorptionsmittel ausgewählt ist aus den Carbiden und Nitriden von Wolfram, Molybdän, Vanadium, Chrom, Tantal und Mischungen derselben, um einen im wesentlichen CO-freien, wasserstoffreichen Gasstrom zu erzeugen,

eine Leitung zur Zuführung eines CO-enhaltenden wasserstoffreichen Gasstroms zu dem Separator,

eine Leitung, die betreibbar den Separator mit dem Anodenkompartiment der Brennstoffzelle zur Abgabe des im wesentlichen CO-freien, wasserstoffreichen Gasstroms daran verbindet, und

eine Leitung zur Zuführung eines Oxidationsmittels zu dem Kathodenkompartiment.

## 8. System nach Anspruch 7, das zwei Separatoren umfaßt.

## 9. System nach Anspruch 7 oder 8, das eine Leitung zur Zuführung eines Spülgases zu dem (jeweiligen) Separator umfaßt, um adsorbiertes CO zu desorbieren.

## 10. System nach einem der Ansprüche 7 bis 9, bei dem das Adsorptionsmittel auf einem Träger vorliegt und/oder trägerlos ist.

## 11. System nach Anspruch 10, bei dem der Träger für das Adsorptionsmittel ausgewählt ist aus einem oder mehreren von Siliciumdioxiden, Aluminiumoxiden, Siliciumdioxid/Aluminiumoxiden, Titanoxiden, Aluminosilikaten und Kohlenstoff.

## 12. System nach einem der Ansprüche 7 bis 11, bei dem das Adsorptionsmittel eine Oberfläche im Bereich von 0,5 bis 200 m<sup>2</sup> pro Gramm aufweist.

## 13. System nach einem der Ansprüche 7 bis 12, bei dem das Adsorptionsmittel Wolframcarbid oder Molybdäncarbid ist.

## Revendications

### 1. Procédé d'élimination de CO d'un courant de gaz

riche en hydrogène contenant du CO pour obtenir un courant de gaz riche en hydrogène sensiblement exempt de CO, comprenant :

le passage du courant de gaz riche en hydrogène contenant du CO à travers un adsorbant capable d'adsorber sélectivement le CO et choisi parmi les carbures et les nitrures de tungstène, de molybdène, de vanadium, de chrome, de tantale et leurs mélanges, de manière à obtenir un courant de gaz riche en hydrogène sensiblement exempt de CO.

### 2. Procédé selon la revendication 1, dans lequel l'adsorbant a une surface spécifique dans la plage de 0,5 à 200 m<sup>2</sup>/g.

### 3. Procédé selon la revendication 1 ou 2, dans lequel l'adsorbant est supporté et/ou non supporté.

### 4. Procédé selon la revendication 3, dans lequel le support de l'adsorbant est choisi parmi un ou plusieurs des silices, des alumines, des silices-alumines, des oxydes de titane, des aluminosilicates et du carbone.

### 5. Procédé selon la revendication 4, dans lequel l'adsorbant est du carbure de tungstène ou du carbure de molybdène.

### 6. Procédé selon l'une quelconque des revendications précédentes, comprenant par ailleurs l'étape de désorption périodique de CO de l'adsorbant au moyen d'un gaz de balayage ou gaz désorbant, ledit gaz étant de préférence non oxydant pour le CO.

### 7. Système de pile à combustible comprenant :

une pile à combustible ayant un compartiment anodique et un compartiment cathodique, au moins un séparateur contenant un adsorbant capable d'adsorber sélectivement le CO d'un courant de gaz riche en hydrogène contenant du CO, ledit adsorbant étant choisi parmi les carbures et les nitrures de tungstène, de molybdène, de vanadium, de chrome, de tantale et de leurs mélanges, pour produire un courant de gaz riche en hydrogène sensiblement exempt de CO,

une conduite pour acheminer un courant de gaz riche en hydrogène contenant du CO au séparateur;

une conduite reliant en fonctionnement le séparateur au compartiment anodique de la pile à combustible pour lui délivrer le courant de gaz riche en hydrogène sensiblement exempt de CO, et

une conduite pour acheminer un agent oxydant au compartiment cathodique.

8. Système selon la revendication 7, comprenant deux desdits séparateurs.
9. Système selon la revendication 7 ou 8, comprenant une conduite pour acheminer un gaz de balayage au séparateur (respectif) pour désorber le CO adsorbé. 5
10. Système selon l'une quelconque des revendications 7 à 9, dans lequel l'adsorbant est supporté et/ou non supporté. 10
11. Système selon la revendication 10, dans lequel le support pour l'adsorbant est choisi parmi une ou plusieurs des silices, des aluminés, des silices-aluminés, des oxydes de titane, des aluminosilicates et du carbone. 15
12. Système selon l'une quelconque des revendications 7 à 11, dans lequel l'adsorbant a une surface spécifique dans la plage de 0,5 à 200 m<sup>2</sup>/g. 20
13. Système selon l'une quelconque des revendications 7 à 12, dans lequel l'adsorbant est le carbure de tungstène ou le carbure de molybdène. 25

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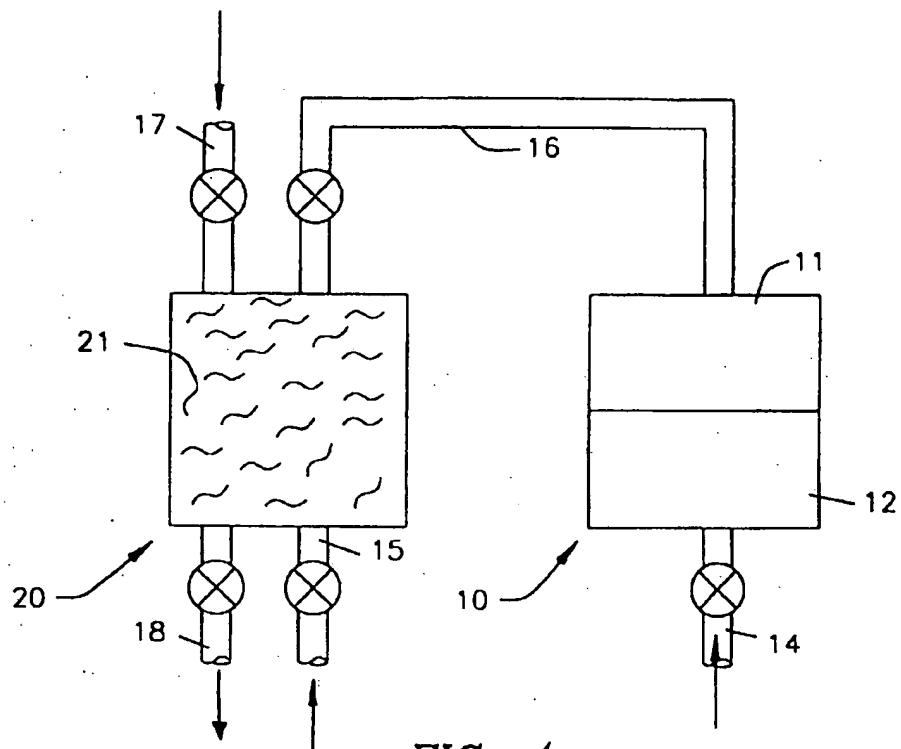


FIG. 1

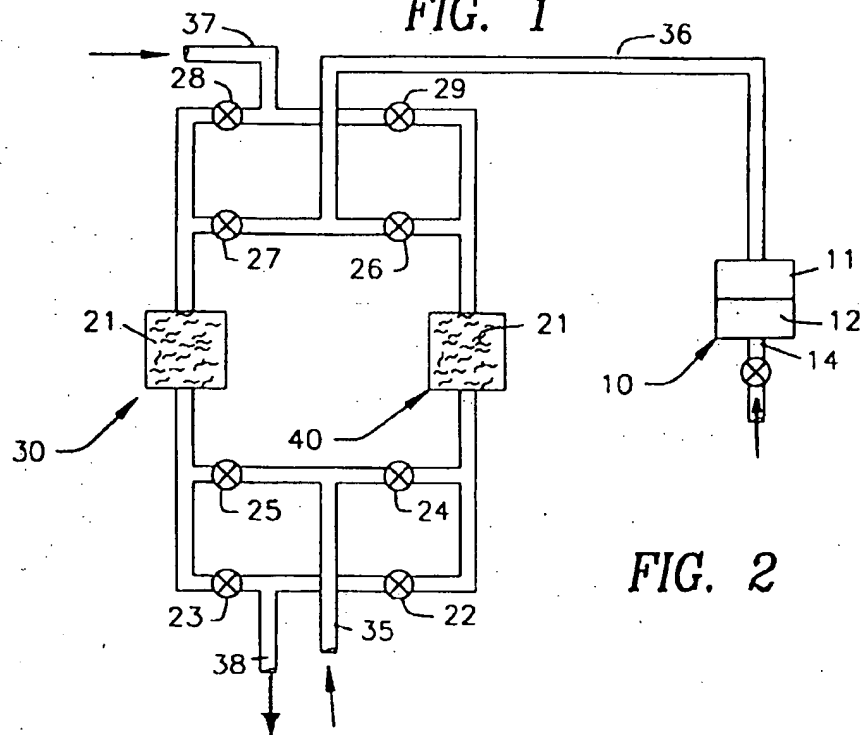


FIG. 2